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(54) Title: ANTIMICROBIAL HAIR TREATMENT COMPOSITION

(57) Abstract

An antimicrobial hair treatment composition comprising: (a) at least one surfactant, (b) particles of an insoluble particulate metal pyrithione in which at least about 50 % by number of the particles are needle shaped particles having a length of between 1 and 50 microns; and (c) a water soluble, cationic polymer wherein the cationic polymer is a deposition aid for the metal pyrithione particles. These hair treatment compositions combine the desirable properties of efficacy against dandruff, stability and aesthetic appeal.

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## ANTIMICROBIAL HAIR TREATMENT COMPOSITION

### Field of the Invention

5 This invention relates to antimicrobial hair treatment compositions for topical application to human hair and scalp for the treatment of, for example, dandruff. In particular, the invention relates to a hair treatment composition comprising a surfactant, water-insoluble antimicrobial  
10 particles and a cationic polymer which serves to enhance the deposition and retention of the particles on the hair and/or the scalp from the composition.

### Background and Prior Art

15 Insoluble particulate metal pyrithiones are acknowledged as antimicrobial agents which can be incorporated into antimicrobial compositions, such as antidandruff hair shampoos and conditioners. The zinc salt (hereinafter  
20 referred to as ZnPTO) is widely used in this context. Generally, dispersed particles of the ZnPTO are suspended in the composition, which is then applied to the hair to deposit the ZnPTO on the hair and scalp.

25 A problem encountered with such compositions is that it is difficult to obtain a stable dispersion containing ZnPTO, since its specific gravity and insolubility leads to precipitation and separation during storage. Steps taken to prevent precipitation and separation of the ZnPTO particles  
30 have hitherto included restriction of the formulational base to highly viscous emulsions or gels, e.g., by incorporation of thickeners or bulking agents to give structural viscosity to the system and prevent ZnPTO settlement. Such an

approach is frequently impractical for shampoo compositions and can give cloudy, aesthetically-inferior products.

Furthermore, the anti-dandruff benefits attainable from particles of ZnPTO incorporated in hair treatment compositions are frequently limited, owing to a poor level of deposition on the intended site; namely the hair and/or the scalp, but particularly the scalp.

10 A further problem encountered with such compositions is that acceptable aesthetic properties, such as pearlescence, of the compositions are often difficult to achieve. The general approach taken to improve the pearlescence is to incorporate pearlescent materials such as ethylene glycol distearate in the compositions. However such an approach alone is frequently dissatisfactory owing to the presence of metal pyrithione particles interfering with the ability of the pearlescent materials to deliver acceptable pearlescence. To address this problem, the prior art teaches that ZnPTO crystals having a flat plate-like morphology interfere less with pearlescers in such compositions. For example EP 34385 describes an aesthetically improved anti-dandruff hair care composition comprising flat, platelet shaped ZnPTO crystals. JP 25 8283242A describes a "mica like" shaped 1-hydroxy-2-pyridinethione heavy metal salt for use in hair care compositions. The mica shaped crystals are said not to impede pearlescence.

30 There continues to be a need, however, for alternative antimicrobial hair treatment compositions to effectively address the above-mentioned problems and particularly which

combine the properties of efficacy, stability and aesthetic appeal.

It has now been found that antimicrobial hair treatment compositions which have good mechanical stability, good optical properties and excellent anti-dandruff ability can be obtained by utilising needle-shaped particles of insoluble particulate metal pyrithione in combination with a deposition aid.

#### Summary of the Invention

Accordingly, in one aspect the present invention provides an antimicrobial hair treatment composition comprising:

- (a) at least one surfactant
- (b) particles of an insoluble particulate metal pyrithione in which at least about 50% by number of the particles are needle shaped particles having a length of between 1 and 50 microns; and
- (c) a water soluble, cationic polymer wherein the cationic polymer is a deposition aid for the metal pyrithione particles.

According to a second aspect the invention also provides a method of treating dandruff comprising applying to the hair a composition according to the first aspect of the present invention.

According to a further aspect of the present invention there is provided the use, in an antimicrobial hair treatment composition, of particles of an insoluble particulate metal

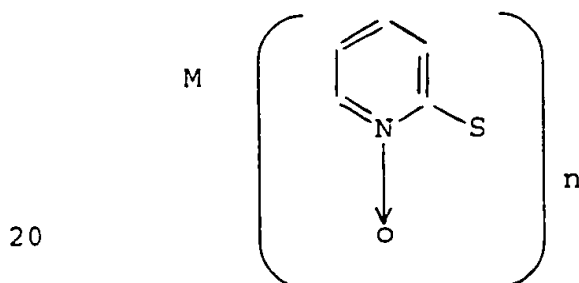
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pyrithione in which at least 50% by number of the particles are needle shaped particles having a length of between 1 and 50 microns.

- 5 According to a still further aspect of the present invention there is provided the use of particles of an insoluble particulate metal pyrithione in which at least 50% by number of the particles are needle shaped particles having a length of between 1 and 50 microns for improving pearlescence of an antimicrobial hair treatment composition.
- 10

#### Detailed Description and Preferred Embodiments

- The insoluble particulate metal pyrithione may be represented by the following general formula:
- 15



in which M is a polyvalent metal ion and n corresponds to the valency of M.

- 25 Preferred examples of M include magnesium, barium, strontium, zinc, cadmium, tin and zirconium. Especially preferred is zinc.

- 30 The term "needle-shaped" particle used herein is used to describe a generally elongate three dimensional particle of any transverse cross-sectional shape, the particle having one dimension, the length, substantially greater than the other two. By "substantially" is meant greater by a factor

of at least two, preferably at least 3 and most preferably at least 5. Although the cross-sectional shape of the particle is not particularly critical it is typically polygonal.

5

The needle-shaped particles of metal pyrithione have a size distribution in which at least about 50% of the particles, by number of the particles, have a length of between 1 and 50 microns. Preferably, the size distribution is such that  
10 at least about 50% of the particles, by number of the particles, have a length of between 2 and 40 microns; most preferably between 4 and 30 microns and even more preferably between 5 and 15 microns; the most preferred length being between 10 and 15 microns. In an even more preferred  
15 embodiment the size distribution is such that at least about 70% of the particles, by number of the particles, have a length of between 2 and 40 microns; most preferably between 4 and 30 microns and even more preferably between 5 and 15 microns; the most preferred length is between 10 and 15  
20 microns. In the most preferred embodiment the size distribution is such that at least about 80% of the particles, by number of the particles, have a length of between 2 and 40 microns; most preferably between 4 and 30 microns and even more preferably between 5 and 15 microns;  
25 the most preferred length being between 10 and 15 microns. The dimensions of the needle shaped particles can be determined most conveniently visually using an electron microscope.

30 The amount of metal pyrithione incorporated into the compositions of the invention may depend on the type of composition and the exact nature of the material used. A preferred amount of metal pyrithione is from about 0.001 to

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about 5% by weight of the total composition, more preferably from about 0.05 to about 3% by weight, most preferably between 0.1 and 1%.

## 5 Preparation Process

The needle-shaped particles of a metal pyrithione may be prepared by mixing a water-soluble salt of pyrithione (such as sodium pyrithione) and a dispersant (such as DARVAN 1, a dispersant which is the sodium salt of polymerized alkyl naphthalene sulphonic acid) while maintaining stirring of this mixture at a temperature of between 20 and 60 degrees Celsius. The stirring is suitably effected using a paddle mixer having a paddle speed of from 50 to 150 rpm. The amount of dispersant added should be sufficient to provide from about 0.05 to about 10% by weight of dispersant, based on the total weight of the final reaction mixture. An aqueous solution of a polyvalent metal salt (for example a zinc salt such as zinc sulphate monohydrate) is then gradually added to the reaction mixture while continuing mixing at the specified paddle speed. Preferably, the amount of polyvalent metal salt is used in a slight (such as 5%) stoichiometric excess, relative to the amount of water-soluble pyrithione salt employed.

The temperature of the reaction mixture should be maintained at between 20 and 60 degree Celsius, and stirring of the reaction mixture continued until all of the polyvalent metal salt solution has been added and a precipitate forms. The resulting rods and needles of insoluble zinc pyrithione salt are collected by vacuum filtration and washed in cold water. The rods and needles of ZnPTO produced by this method are generally about 0.1 to 1.0 microns width and 1 to 50 microns in length.



The composition according to the invention also comprises at least one surfactant, preferably chosen from anionic, cationic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof.

A particularly preferred hair treatment composition in accordance with the invention is a shampoo composition in which at least one surfactant provides a deterging benefit.

10 The deterging surfactant is preferably selected from anionic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof.

Suitable anionic surfactants include the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from one to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauroyl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are

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sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

5

Nonionic surfactants suitable for use in compositions of the invention may include condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups. Other suitable nonionics include mono- or di-alkyl alkanolamides. Example include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

15 Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycines, alkyl carboxyglycines, alkyl amphopropionates, 20 alkylamphoglycines alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl 25 betaine and sodium cocamphopropionate.

The surfactants are present in shampoo compositions of the invention in an amount of from 0.1 to 50% by weight of the composition, preferably from 0.5 to 30% by weight.

30

Hair treatment compositions in accordance with the invention may also take the form of hair conditioning compositions, which preferably comprise one or more cationic surfactants.

The use of cationic surfactants is especially preferred, because these ingredients are capable of providing conditioning benefits to hair.

5 Examples of cationic surfactants include:

quaternary ammonium hydroxides, e.g., tetramethylammonium hydroxide, alkyltrimethylammonium hydroxides wherein the alkyl group has from about 8 to 22 carbon atoms, for example  
10 octyltrimethylammonium hydroxide, dodecyltrimethylammonium hydroxide, hexadecyltrimethylammonium hydroxide, cetyltrimethylammonium hydroxide, octyldimethylbenzylammonium hydroxide, decyldimethylbenzylammonium hydroxide, stearyldimethylbenzylammonium  
15 hydroxide, didodecyldimethylammonium hydroxide, dioctadecyldimethylammonium hydroxide, tallow trimethylammonium hydroxide, cocotrimethylammonium hydroxide, and the corresponding salts thereof, e.g., chlorides  
20 Cetylpyridinium hydroxide or salts thereof, e.g., chloride  
Quaternium -5  
Quaternium -31  
Quaternium -18  
and mixtures thereof.

25

In hair conditioning compositions according to the invention, the level of cationic surfactant is preferably from 0.01 to 10%, more preferably 0.05 to 5%, most preferably 0.1 to 2% by weight of the composition.

30

Hair treatment compositions of the invention may also contain one or more conditioning agents, preferably selected from silicones, protein hydrolyzates and quaternised protein

- 10 -

hydrolysates and other materials which are known in the art as having desirable hair conditioning properties.

Silicones are the most preferred conditioning agents.

5

Suitable silicones include volatile and non-volatile silicones, such as for example polyalkylsiloxanes, polyalkylaryl siloxanes, siloxane gums and resins, cyclomethicones, aminofunctional silicones, quaternary  
10 silicones and mixtures thereof. Silicone oil is a particularly preferred conditioning agent for hair. The silicone may be in the form of a low viscosity oil which may contain a high viscosity oil or gum in solution.

Alternatively, the high viscosity material may be in the  
15 form of an emulsion in water. The emulsion may be of high viscosity oil or of a solution of gum in a lower viscosity oil. The particle size of the oil phase may be anywhere in the range from 30 nanometres to up to 20 microns average size.

20

The silicone oil may suitably be a polydimethylsiloxane with an average particle size of less than 20 microns and preferably less than 2 microns. Small particle size enables a more uniform distribution of silicone conditioning agent  
25 for the same concentration of silicone in the composition. Advantageously, a silicone with a viscosity in the range 1-20 million cst is used. The silicone can be cross-linked.

Suitable protein hydrolysates include lauryl dimonium  
30 hydroxy propylamino hydrolysed animal protein, available commercially under the trade name LAMEQUAT L, and hydrolysed keratin containing sulphur-bearing amino acids, available commercially under the trade name CROQUAT WKP.

In accordance with the invention, the hair treatment composition also comprises a polymeric water-soluble cationic polymer as a deposition aid for the needle-shaped particles. The term "deposition aid" is defined herein as  
5 an agent which enhances deposition of the needle-shaped particles of metal pyrithione on the intended site, i.e., the hair and/or the scalp.

The deposition aid will generally be present at levels of  
10 from 0.01 to 5%, preferably from about 0.05 to 1%, more preferably from about 0.08% to about 0.5% by weight.

Preferably the cationic charge density, which is defined as the reciprocal of the molecular weight of a monomeric unit  
15 of the polymer containing 1 charge is at least 0.1 meq/g, preferably above 0.8 or higher. The cationic charge density should not exceed 4 meq/g, it is preferably less than 3 and more preferably less than 2 meq/g. The charge density can be measured using conductimetric analysis and should be  
20 within the above limits at the desired pH of use, which will in general be from about 3 to 9 and preferably between 4 and 8.

Preferred deposition aids are cationic derivatives of guar  
25 gum and cationic polyacrylamides.

Suitable cationic derivatives of guar gum are JAGUAR C13S, which has a low degree of substitution of the cationic groups and high viscosity. JAGUAR C15, having a moderate  
30 degree of substitution and a low viscosity, JAGUAR C17 (high degree of substitution, high viscosity), JAGUAR C16, which is a hydroxypropylated cationic guar derivative containing a low level of substituent groups and JAGUAR 162 which is a

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high transparency, medium viscosity guar having a low degree of substitution. Particularly preferred deposition aids are Jaguar C13S with a cationic charge density of 0.8 meq/g.

- 5    Suitable cationic polyacrylamides are described in WO 95/22311 whose contents are incorporated herein by reference.

The composition may further comprise from 0.1 to 5 % of a  
10    suspending agent. Examples are polyacrylic acids, cross linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters,  
15    heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearates, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Polyacrylic acid is available commercially as  
20    Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used, they are available commercially as Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic  
25    acid containing a monomer and acrylic acid esters is Carbopol 1342. All Carbopol materials are available from Goodrich and Carbopol is a trade mark. A further suitable suspending agent is dihydrogenated tallow phthalic acid amide (available from Stepan under the trademark Stepan TAB-  
30    2).

Suitable cross linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable

heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

Another ingredient that may advantageously be incorporated  
5 into hair treatment compositions of the invention is a fatty alcohol material. The use of these materials is especially preferred in conditioning compositions of the invention, in particular conditioning compositions which comprise one or more cationic surfactant materials. The combined use of  
10 fatty alcohol materials and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a lamellar phase, wherein the cationic surfactant is dispersed.

15

Preferred fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 20. Examples of preferred fatty alcohols are cetyl alcohol and stearyl alcohol. The use of these materials is also advantageous in that they contribute  
20 to the overall conditioning properties of compositions of the invention.

The level of fatty alcohol materials is conveniently from 0.01 to 10%, preferably from 0.1 to 5% by weight of the  
25 composition. The weight ratio of cationic surfactant to fatty alcohol is preferably from 10:1 to 1:10, more preferably from 4:1 to 1:8, most preferably from 1:1 to 1:4.

A further ingredient that may be desirably included in the  
30 hair treatment composition is a pearlescent material. Suitable pearlescent materials include ethylene glycol distearate, ethylene glycol monostearate, guanine and titanium dioxide coated micas, bismuth oxychloride, and

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stearic monoethanol amide. The level of pearlescent material present in the composition is generally 0.1% to 5%, preferably from 0.3% to 3% by weight of the composition.

- 5 The hair treatment compositions of the invention are preferably aqueous based. The compositions suitably comprise water in amount of from about 20 to about 99% by weight of the total composition.
- 10 The compositions of the invention are preferably rinse-off compositions, i.e., suitable for applying to the hair and/or scalp, left thereon for an appropriate period of time and then rinsed off with water. Thus, shampoos and conditioners are a particularly preferred product form for compositions
- 15 of the invention.

Depending on the type of composition employed, one or more additional ingredients conventionally incorporated into hair treatment formulations may be included in the compositions

20 of the invention. Such additional ingredients additional antimicrobial agents, foam boosters, perfumes, colouring agents, preservatives, thickeners, viscosity modifiers, proteins, polymers, buffering or pH adjusting agents, moisturising agents, herb or other plant extracts and other

25 natural ingredients.

The invention is further illustrated by way of the following non-limitative examples, in which all percentages are by weight based on total weight of the composition, unless

30 otherwise specified.



Example 1

The shape and size of the particles of ZnPTO prepared as described hereinbefore under the heading "Preparation  
5 Process" were determined using electron microscopy in the following manner.

A sample of ZnPTO particles prepared as described hereinbefore was shaken thoroughly and 10 microlitres was  
10 removed by pipette and diluted with 18 mililitres of water. A small amount of the diluted sample was placed onto an aluminium stub and left to air dry for two hours afterwhich the stub plus diluted sample was placed under vacuum for 48  
15 hours. The samples were then coated with gold Ca 5nm to aid conductivity before imaging at 10kv. Ten photographic images of the sample were taken. Total number (T) of whole needles in each photograph were counted and measured. Those  
20 particles having a length of between 1 and 50 microns, which dimension was substantially greater than its other two, represented "needle-shaped particles" (N) as defined hereinbefore. The percentage by number of the particles in the sample that were needle-shaped particles having a length of between 1 and 50 microns was accordingly determined by the calculation  $(N/T) \times 100$ .

25

Example 2

Comparative Assessment of Pearlescence of Shampoos

The pearlescence of shampoo formulations in accordance with  
30 the present invention were investigated in the following experiment.

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Protocol

All the test shampoos were made from a common base, namely 14 % sodium lauryl ether sulphate (2EO), 2% cocamidopropylbetaine, 0.1 % JAGUAR C13S (guar hydroxypropyltrimonium chloride, ex Rhodia), 6% pearlising agent Mirasheen CP 820, ex Rhodia and suspending, colouring and preserving agents. The following ZNPTO particles were additionally added to the test shampoos A to E.

10

Shampoo	ZNPTO Particle Size and Shape	%
A	0.5 micron diameter sphere	0.3
B	5 micron length needle	0.3
15 C	0.5 micron diameter sphere	0.5
D	5 micron diameter sphere	0.5
E	5 micron length needle	0.5

Shampoos B and E contain ZnPTO particles in which at least 50% by number thereof are ZnPTO needles according to the present invention. Shampoos A, C, and D contain standard size ZnPTO particles ex Olin and thus serve as comparative examples outside the present invention.

25 20g of each shampoo was poured into a separate Petri dish size 15 x 100 mm and placed on white paper. A spatula was used to make a line on the surface of the shampoo. The samples were left for 30 seconds prior to visual assessment. A number was assigned to each shampoo to represent the level of pearlescence depending on the effect observed according to the following scale:

30

Effect Observed

Scale of  
Pearlescence

	No line visible	0 (Poor)
5	Line visible but unclear	1 (Fair)
	Sharp Line Visible	2 (Good)

Results

10	Shampoo	Scale of Pearlescence
	A	1
	B	2
	C	0
	D	1
15	E	2

The results show that the pearlescence of shampoo composition B containing needle-shaped ZnPTO is better than composition A, identical to B except for containing prior art ZnPTO particles. The results also show that composition E containing needle-shaped ZnPTO particles is better than compositions C and D, identical to E except for containing prior art ZnPTO particles.

25 Examples 3

Hair shampoo compositions in accordance with the present invention, comprising needle-shaped particulate metal pyrrithione and a deposition polymer were prepared using techniques well known in the art. The ZnPTO particles were prepared as described herein. The composition had the following formulation.

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<u>INGREDIENT</u>	<u>% BY WEIGHT</u>
<u>EXAMPLE 1</u>	
5	
Sodium lauryl ether sulphate 2EO (70% active)	20
Cocamidopropyl betaine (30% active)	6.6
10	
Jaguar C13S	0.1
ZnPTO, needle-shaped particle (25% active) (5 micron length)	2
15	
CARBOPOL 980	0.5
Ethylene glycol distearate	8.0
20	
Dimethicone (60% aqueous emulsion)	1.67
Vitamin E acetate	0.05
25	
Preservative, colour, fragrance	- q.s. -
Water	- to 100% -
30	

This shampoo gave excellent anti-dandruff performance on the hair, had a good pearlescent quality and was stable without visible signs of separation after three months storage both at room temperature and at 45° C.

CLAIMS

1. An antimicrobial hair treatment composition comprising:  
5 (a) at least one surfactant  
  
(b) particles of an insoluble particulate metal  
pyrithione in which at least about 50% by number  
10 of the particles are needle shaped particles  
having a length of between 1 and 50 microns; and  
  
(c) a water soluble, cationic polymer wherein the  
cationic polymer is a deposition aid for the metal  
15 pyrithione particles.
2. A composition according to claim 1 wherein metal  
pyrithione is zinc pyrithione.
- 20 3. A composition according to any preceding claim wherein  
the metal pyrithione is present in the composition in  
an amount of from 0.05 to 3% by weight of the  
composition.
- 25 4. A composition according to any preceding claim wherein  
at least about 50% by number of the particles have a  
length of between 2 and 40 microns, preferably between  
4 and 30 microns, most preferably between 10 and 15  
microns.
- 30 5. A composition according to any preceding claim wherein  
it comprises from 0.1% to 5% by weight of the  
composition of a pearlescent material.

6. A composition according to any preceding claim wherein the cationic polymer is a cationic derivative of guar gum or a cationic polyacrylamide.
- 5 7. A composition according to any preceding claim wherein the composition is a shampoo composition in which at least one surfactant is selected from anionic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof, the total amount of surfactant being  
10 from about 0.1 to about 50% by weight of the composition.
8. A composition according to any preceding claim which further comprises a conditioning agent selected from  
15 volatile and nonvolatile silicones.
9. A method of treating dandruff comprising applying to the hair an antimicrobial composition comprising a composition as claimed in any of claims 1 to 8.  
20
10. Use in an antimicrobial hair treatment composition of particles of an insoluble particulate metal pyrithione in which at least 50% by number of the particles are needle shaped particles having a length of between 1  
25 and 50 microns.
11. Use of particles of an insoluble particulate metal pyrithione in which at least 50% by number of the particles are needle shaped particles having a length  
30 of between 1 and 50 microns for improving pearlescence of an antimicrobial hair treatment composition.

## INTERNATIONAL SEARCH REPORT

International Application No.

EP 99/04154

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A.P.	WO 98 48629 A (OLIN CORP.) 5 November 1998 (1998-11-05) ---	1
A.P.	WO 98 41505 A (OLIN CORP.) 24 September 1998 (1998-09-24) page 19, line 1-17 ---	1
A	WO 95 22905 A (OLIN CORP.) 31 August 1995 (1995-08-31) page 14, line 16-23 ---	1
A	GB 2 311 995 A (OLIN CORP.) 15 October 1997 (1997-10-15) ---	1
A	EP 0 800 814 A (UNILEVER PLC, UNILEVER N.V.) 15 October 1997 (1997-10-15) ---	1
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☒ Further documents are listed in the continuation of box C☒ Patent family members are listed in annex

## Special categories of cited documents

A\* document defining the general state of the art which is not considered to be of particular relevance

E\* earlier document but published on or after the international filing date

L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

C\* document referring to an oral disclosure, use, exhibition or other means

P\* document published prior to the international filing date but later than the priority date claimed

T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X\* document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y\* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

S\* document member of the same patent family

Date of the actual completion of the international search

19 October 1999

Date of mailing of the international search report

17/11/1999

Name and mailing address of the ISA

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Authorized officer

Glikman, J-F



C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication where appropriate of the relevant passages	Relevant to claim No.
A	WO 97 03637 A (UNILEVER PLC. UNILEVER N.V.) 6 February 1997 (1997-02-06) ---	1
A	WO 97 29733 A (JANSSEN PHARMACEUTICA N.V., NEUTROGENA CORP.) 21 August 1997 (1997-08-21) -----	1

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 99/04154

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9848629	A	05-11-1998	AU 7249398 A	24-11-1998
WO 9841505	A	24-09-1998	AU 6680898 A	12-10-1998
WO 9522905	A	31-08-1995	US 5540860 A	30-07-1996
			AU 1926495 A	11-09-1995
			CN 1142173 A	05-02-1997
			EP 0748160 A	18-12-1996
			JP 9506903 T	08-07-1997
			NO 963570 A	27-08-1996
			US 5650095 A	22-07-1997
GB 2311995	A	15-10-1997	AU 2460197 A	07-11-1997
			WO 9739096 A	23-10-1997
EP 800814	A	15-10-1997	CA 2201568 A	12-10-1997
			JP 10036233 A	10-02-1998
WO 9703637	A	06-02-1997	AU 6613596 A	18-02-1997
			BR 9609532 A	23-02-1999
			CA 2226907 A	06-02-1997
			CN 1195283 A	07-10-1998
			EP 0839022 A	06-05-1998
			JP 11509220 T	17-08-1999
			US 5723112 A	03-03-1998
WO 9729733	A	21-08-1997	AU 1769797 A	02-09-1997
			CA 2240526 A	21-08-1997
			CN 1211177 A	17-03-1999
			CZ 9802525 A	16-12-1998
			EP 0884997 A	23-12-1998
			HU 9900581 A	28-07-1999
			NO 982775 A	25-08-1998
			NZ 331380 A	29-06-1999
			PL 328168 A	18-01-1999